(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 568 336 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 93303310.2

(51) Int. Cl.[5]: C07D 301/12

(22) Date of filing: 28.04.93

(30) Priority: 30.04.92 US 876772

(43) Date of publication of application:
03.11.93 Bulletin 93/44

(84) Designated Contracting States:
AT BE DE ES FR GB IT NL

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(54) Epoxidation process using titanium-rich silicalite catalysts.

(57) Olefins are epoxidized by hydrogen peroxide in the presence of a crystalline titanium silicalite zeolite catalyst having a Si:Ti molar ratio in the lattice framework of from 8:1 to 23:1. High yields of epoxides with minimal non-selective loss of either hydrogen peroxide or olefin are realized.

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FIELD OF THE INVENTION:

This invention relates to m thods of poxidizing olefins so as to obtain products containing epoxide functional groups. In particular, the invention pertains to processes wh reby a hydrog n peroxide source is reacted with an ethylenically unsaturated substrate in the presence of a titanium silicalite catalyst containing a high proportion of titanium to yield an epoxide.

BACKGROUND OF THE INVENTION:

Epoxides such as ethylene oxide, propylene oxide, 1,2-butene oxide and the like are useful intermediates for the preparation of a wide variety of products. The oxirane functionality in such compounds is highly reactive and may be ring-opened with any number of nucleophilic reactants. For example, epoxides may be hydrolyzed to yield glycols useful as anti-freeze components or reactive monomers for the preparation of condensation polymers such as polyesters.

Polyether polyols generated by the ring-opening polymerization of epoxides are widely utilized as intermediates in the preparation of polyurethane foams, elastomers, sealants, coatings, and the like. The reaction of epoxides with alcohols provides glycol ethers, which may be used as polar solvents in a number of applications.

Many different methods for the preparation of epoxides have been developed. One such method involves the use of certain titanium silicalite compounds to catalyze olefin oxidation by hydrogen peroxide. This method is described, for example, in Huybrechts et al., J. Mol. Catal. **71**, 129(1992), U.S. Pat. Nos. 4,824,976 (Clerici et al.) and 4,833,260 (Neri et al.) European Pat. Pub. Nos. 311,983, 190,609, 315,247 and 315,248, Belgian Pat. Pub. No. 1,001,038, Clerici et al., J. Catal. **129**, 159(1991), and Notari, in "Innovation in Zeolite Material Science," Studies in Surface Science and Catalysis, Vol. 37, p. 413 (1988). The titanium silicalite compounds which have heretofore been found to be useful as epoxidation catalysts are synthetic zeolites corresponding to the general chemical formula

$$xTiO_2(1 - x)SiO_2$$

wherein x must be in the range of from 0.0001 to 0.04. Expressed a different way, it has been thought that the molar ratio of Si:Ti must be no less than 24:1 in order for such substances to function effectively as catalysts in the hydrogen peroxide oxidation of olefins to epoxides. The low concentration of titanium in these materials indicates that they are silicalites in which a limited number of titanium atoms have taken the place of silica in the lattice framework. Thus, the titanium atoms are isolated from each other by long

$$\left[-O-\overset{|}{\underset{|}{Si}}- \right]_n$$

sequences. The prior art teaches that as the proportion of titanium relative to silica in a titanium silicalite is increased, a greater number of titanium atoms in close proximity to other titanium atoms will be present in the lattice framework. Since the epoxidation activity of the titanium silicalite is believed to be due to isolated titanium atoms, whereas the non-selective decomposition of hydrogen peroxide to water and oxygen (i.e., without transfer of oxygen to the olefin) is thought to take place at titanium atoms located in close proximity to each other, the effective use of titanium-rich silicalites as epoxidation catalysts has not heretofore been thought to be feasible. Titanium silicalites containing a relatively high proportion of titanium to silicon would thus have been expected to perform unsatisfactorily in epoxidation reactions since selectivity to epoxide would be significantly lower.

Huybrechts et al. [J. Mol. Catal., **71**, 129(1992)], for example, have reported that an attempt to epoxidize 1-octene using hydrogen peroxide and a titanium silicalite containing 4 mole % titanium (Si:Ti = 24) gave a total of only 61% selectivity based on hydrogen peroxide to organic oxidation products. The inefficient use of hydrogen peroxide was ascribed to its decomposition to water and oxygen. Higher selectivities were observed using catalysts containing lower levels of titanium. The conversion of 1-octene was also lower than expected from the activity of silicalites containing lower levels of titanium.

Th mechanism by which titanium silicalites catalyze the reaction of hydrogen peroxide with organic substrates is not well und rstood and the utcome of such reactions is highly unpredictable. For xample, when an olefin is reacted with hydrog n peroxide in the presence of titanium silicalite, the product obtained may be eith r epoxid (U.S. Pat. No. 4,833,260), glycol eth r (U.S. Pat. No. 4,476,327), r glycol (Example 10 of U.S. Pat. No. 4,410,501).

SUMMARY OF THE INVENTION:

Contrary to the expectation of the pri r art, it has now been discovered that titanium silicalite zeolites containing high proportions of titanium are extremely productive catalysts for th conversion of ethyl nically unsaturated substrates to epoxides using hydrogen peroxide as a source of oxygen. Remarkably high selectivities to epoxide are realized with minimal non-productive hydrogen peroxide decomposition or organic by-product formation.

This invention provides a process for producing an epoxide comprising contacting an olefin with a hydrogen peroxide source in the presence of a catalytically effective amount of a titanium silicalite zeolite having a Si:Ti molar ratio in the lattice framework of said zeolite of from 8:1 to 23:1 for a time and at a temperature effective to convert the olefin to epoxide.

DETAILED DESCRIPTION OF THE INVENTION:

In the process of this invention, an olefin is epoxidized using a source of hydrogen peroxide (H_2O_2) as an oxidizing agent. It has now been unexpectedly discovered that the use of a titanium-rich silicalite catalyst having a Si:Ti molar ratio in the lattice framework of the catalyst of from 8:1 to 23:1 results in the rapid and highly selective formation of epoxide with minimal loss of the hydrogen peroxide through non-selective decomposition. This discovery was unexpected in view of the teaching of the prior art that titanium silicalites having a high proportion of titanium atoms in close proximity to each other would perform poorly as epoxidation catalysts.

The preparation of titanium silicalites suitable for use in the process of this invention is described, for example, in Thangaraj et al., J. Catal. **130**, 1(1991), the teachings of which are incorporated herein by reference in their entirety. Typically, a hydrolyzable organosilicate such as tetraalkyl orthosilicate is first partially hydrolyzed by combining with an aqueous solution of a quaternary ammonium salt (preferably, the hydroxide salt). The amount of water employed is from 25% to 75% of the amount theoretically required to completely hydrolyze the organosilicate. The resulting partially hydrolyzed mixture is then combined with a titanium alkoxide or other hydrolyzable titanium compound. The molar ratio of silicon to titanium in the final catalyst may be readily controlled as desired by varying the relative proportions of organosilicate and titanium alkoxide employed. To attain a high degree of titanium incorporation in the lattice framework, it is desirable to dissolve the titanium alkoxide in an anhydrous organic solvent prior to combining with the partially hydrolyzed mixture and to employ a titanium alkoxide such as titanium tetrabutoxide which has a relatively slow rate of hydrolysis. The anhydrous organic solvent may be an alcohol such as isopropyl alcohol. Preferably, the hydrolysis rate of the organosilicate and the titanium alkoxide are substantially equivalent. An additional portion of the quaternary ammonium salt solution is then added to complete the hydrolysis. The alcohol generated during the hydrolysis steps may then be removed by heating at a slightly elevated temperature (e.g., 50-100°C) to yield an initial gel. The initial gel is then allowed to crystallize at a temperature of from 125 to 225°C for a period of 1 to 7 days. The crystalline titanium silicalite thus obtained is thereafter calcined at 450-650°C. The catalyst may be treated with an alkaline substance or a silylating agent so as to reduce the surface acidity, in analogy to the methods described in U.S. Pat. No. 4,937,216 for low titanium-content titanium silicalites (the teachings of this patent are incorporated herein by reference in their entirety).

The crystal form of the titanium-rich silicalite catalyst may be varied as desired by selecting different quaternary ammonium salts for use during the preparation of said catalyst. As is well known in the art, the pore size, channel structure, and topology of such catalysts and arrangement of metal atoms in the zeolite framework are influenced by the size and shape of the quaternary ammonium salt. The quaternary ammonium salt thus functions as a template or crystal-directing agent and may, for example, be selected from salts wherein the cation is tetra n-propyl ammonium, tetra n-butyl ammonium, tetraethyl ammonium, tetramethyl ammonium, methyl tri-n-butyl ammonium, triethyl methyl ammonium, n-hexyl trimethyl ammonium, trimethyl ammonium, trimethyl neopentyl ammonium, phenyl trimethyl ammonium, benzyl triethyl ammonium, n-dodecyl trimethyl ammonium, benzyl tri-n-propyl ammonium, tetra n-pentyl ammonium, ethyl pyridinium, diethyl piperidinium, tetra-n-hexyl ammonium, tetra-n-octyl ammonium, tetra-n-dodecyl ammonium, trimethyl ethanol ammonium hydroxide, and the like and combinations thereof and well as any other quaternary ammonium salts known in the art to be useful in the preparation of synthetic zeolites or molecular sieves.

Titanium-rich silicalite catalysts particularly preferred for use in the process f this invention includ those substances having an MFI structure (i. ., a topology similar to that exhibited by th ZSM-5 aluminosilicate z olit s) as well as substances having an MEL structure (i. ., a top logy similar to that xhibited by th ZSM-11 aluminosilicate zeolites). Other useful catalysts includ titanium-rich silicalites having CAN, FAU, FER, TON, LTA, MTT, MTW, r MAZ topologies.

Preferably, ess ntially all of the titanium present is in the zeolite-like lattice framework. Th catalyst itself pref rably does not contain any appreciabl am unt f any amorphous phase or a crystallin phase other than the crystallin titanium silicalite phase. As will be xplained subsequ ntly, however, the use of a binder or support in combination with the titanium silicalite may be advantageous under certain circumstances.

Catalysts suitable for use in the process of this invention will have a composition corresponding to the following empirical formula

$$xTiO_2\cdot(1 - x)\,SiO_2$$

where x is between 0.045 and 0.125 (more preferably, between 0.050 and 0.105).

The amount of catalyst employed is not critical, but should be sufficient so as to substantially accomplish the desired epoxidation reaction in a practicably short period of time. The optimum quantity of catalyst will depend upon a number of factors including reaction temperature, olefin reactivity and concentration, hydrogen peroxide concentration, type and concentration of organic solvent as well as catalyst activity. Typically, however, the amount of catalyst will be from 0.01 to 10 grams per mole of olefin. The concentration of titanium in the total epoxidation reaction mixture will generally be from about 10 to 10,000 ppm.

The catalyst may be utilized in powder, pellet, microspheric, monolithic or any other suitable physical form. The use of a binder (co-gel) or support in combination with the titanium-rich silicalite may be advantageous. Supported or bound catalysts may be prepared by the methods known in the art to be effective for zeolite catalysts in general.

Illustrative binders and supports include silica, alumina, silica-alumina, silica-titania, silica-thoria, silica-magnesia, silica-zironia, silica-beryllia, and ternary compositions of silica with other refractory oxides. Also useful are clays such as montmorillonites, koalins, bentonites, halloysites, dickites, nacrites, and ananxites. The proportion of titanium silicalite:binder or support may range from 99:1 to 1:99, but preferably is from 5:95 to 80:20. The methods described in U.S. Pat. No. 4,701,428 (incorporated herein by reference in its entirety) may be adapted for the preparation of microspheres containing oligomeric silica binder and titanium-rich silicalite crystals which are suitable and preferred for use in the process of this invention.

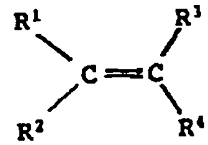
The olefin substrate epoxidized in the process of this invention may be any organic compound having at least one ethylenically unsaturated functional group (i.e., a carbon-carbon double bond) and may be an aromatic, aliphatic, mixed aromatic-aliphatic (e.g., aralkyl), cyclic, branched or straight chain olefin. Preferably, the olefin contains from 2 to 30 carbon atoms (i.e., a C_2-C_{30} olefin). More than one carbon-carbon double bond may be present in the olefin; dienes, trienes, and other polyunsaturated substrates thus may be used. Other examples of suitable substrates include unsaturated fatty acids or fatty acid derivatives such as esters or glycerides and oligomeric or polymeric unsaturated compounds such as polybutadiene.

The olefin may contain substituents other than hydrocarbon substituents such as halide, carboxylic acid, ether, hydroxy, thiol, nitro, cyano, ketone, acyl, ester, anhydride, amino, and the like.

Exemplary olefins suitable for use in the process of this invention include ethylene, propylene, the butenes, butadiene, the pentenes, isoprene, 1-hexene, 3-hexene, 1-heptene, 1-octene, diisobutylene, 1-nonene, 1-tetradecene, pentamyrcene, camphene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, the trimers and tetramers of propylene, polybutadiene, polyisoprene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, cyclododecatriene, dicyclopentadiene, methylenecyclopropane, methylenecyclopentane, methylenecyclohexane, vinylcyclohexane, vinyl cyclohexene, methallyl ketone, allyl chloride, allyl bromide, acrylic acid, methacrylic acid, crotonic acid, vinyl acetic acid, crotyl chloride, methallyl chloride, the dichlorobutenes, allyl alcohol, allyl carbonate, allyl acetate, alkyl acrylates and methacrylates, diallyl maleate, diallyl phthalate, unsaturated triglycerides such as soybean oil, and unsaturated fatty acids, such as oleic acid, linolenic acid, linoleic acid, erucic acid, palmitoleic acid, and ricinoleic acid and their esters (including mono-, di-, and triglyceride esters), and alkenyl aromatic compounds such as styrene, α-methyl styrene, β-methyl styrene, divinyl benzene, 1,2-dihydronaphthalene, indene, stilbene, cinnamyl alcohol, 2-methyl-1-phenyl-1-propene, 2-methyl-3-phenyl-2-propen-1-ol, cinnamyl acetate, cinnamyl bromide, cinnamyl chloride, 4-stilbenemethanol, ar-methyl styrene, ar-ethyl styrene, ar-tert-butyl styrene, ar-chlorostyrene, 1,1-diphenylethylene, vinyl benzyl chloride, vinyl naphthalene, vinyl benzoic acid, ar-acetoxy styrene, ar-hydroxy styrene (i.e., vinyl phenol), 2- or 3-methyl indene, 2,4,6-trimethylstyrene, 1-phenyl-1-cyclohexene, 1,3-diisopropenyl benzene, vinyl anthracene, vinyl anisole, and the like.

Mixtures of olefins may be epoxidized and the resulting mixture of epoxides either employed in mixed form or separat d into th diff rent compon nt epoxides.

The process of this inv ntion is specially useful for th epoxidation of C_2-C_{30} ol fins having the g neral structure



wherein R^1, R^2, R^3, and R^4 are the same or different and are selected from the group consisting of hydrogen, C_1-C_{20} alkyl, C_5-C_{12} cycloalkyl, C_6-C_{20} alkyl cycloalkyl, C_6-C_{20} aryl, and C_7-C_{20} aryl alkyl (i.e., an alkyl group bearing at least one aryl substituent such as benzyl or phenethyl).

The oxidizing agent employed in the process of this invention is a hydrogen peroxide source such as hydrogen peroxide (H_2O_2) or a hydrogen peroxide precursor (i.e., a compound which under the epoxidation reaction conditions is capable of generating hydrogen peroxide).

The amount of hydrogen peroxide relative to the amount of olefin is not critical, but most suitably the molar ratio of hydrogen peroxide:olefin is from about 100:1 to 1:100 when the olefin contains one ethylenically unsaturated group. The molar ratio of ethylenically unsaturated groups in the olefin substrate to hydrogen peroxide is more preferably in the range of from 1:10 to 10:1. One equivalent of hydrogen peroxide is theoretically required to oxidize one equivalent of a mono-unsaturated olefin substrate, but it may be desirable to employ an excess of one reactant to optimize selectivity to the epoxide. A key advantage of the process of this invention as compared to other epoxidation processes is that neither a large molar excess of hydrogen peroxide relative to olefin or a large molar excess of olefin relative to hydrogen peroxide is required. High yields of epoxide may be realized using a slight (i.e., 5-75%) molar excess of olefin relative to hydrogen peroxide (i.e., the molar ratio of olefin to hydrogen peroxide is from 1.05:1 to 1.75:1). The hydrogen peroxide is thus used in a very efficient manner; little of the hydrogen peroxide is wasted through non-selective decomposition to water (i.e., without oxidation of an olefin molecule). Since hydrogen peroxide is relatively costly to generate, this means that the process of the invention may be economically practiced on a commercial scale. Additionally, processing costs arising from recovering and recycling of olefin are minimized since there is no need to employ a large excess of olefin in order to optimize epoxide selectivity, in contrast to known epoxidation processes employing organic hydroperoxides and molybdenum-containing catalysts.

Although the hydrogen peroxide to be utilized as the oxidizing agent may be derived from any suitable source, a distinct practical advantage of the process of this invention is that the hydrogen peroxide may be obtained by contacting an aryl-substituted secondary alcohol such as α-methyl benzyl alcohol with molecular oxygen under conditions effective to form an oxidant mixture comprised of secondary alcohol and hydrogen peroxide. Typically, such an oxidant mixture will also contain an aryl-substituted ketone such as acetophenone corresponding to the secondary alcohol (i.e., having the same carbon skeleton), minor amounts of water, and varying amounts of other active oxygen species such as organic hydroperoxides. The use of oxidant mixtures of this type in an integrated olefin epoxidation process employing titanium silicalite catalysts is described in more detail in our copending European patent application No. filed on the same day as this application and entitled "Integrated Process For Epoxide Production" (Agent's reference 17273).

If desired, a solvent may additionally be present during the epoxidation process of this invention in order to dissolve the reactants other than the zeolite catalyst, to provide better temperature control, or to favorably influence the epoxidation rates and selectivities. The solvent, if present, may comprise from 1 to 99 weight percent of the total epoxidation reaction mixture and is preferably selected such that it is a liquid at the epoxidation reaction temperature. Organic compounds having boiling points at atmospheric pressure of from abut 50°C to 300°C are generally preferred for use. Illustrative examples of suitable solvents include, but are not limited to, ketones (e.g., acetone, methyl ethyl ketone, acetophenone), ethers (e.g., tetrahydrofuran, butyl ether), nitrile (e.g., acetonitrile), aliphatic and aromatic hydrocarbons, halogenated hydrocarbons, and alcohols (e.g., methanol, ethanol, isopropyl alcohol, t-butyl alcohol, α-methyl benzyl alcohol, cyclohexanol). More than one type of solvent may be utilized. For example, the use of methanol as a co-solvent when an aryl-substituted secondary alcohol such as α-methyl benzyl alcohol is the main solvent has been found to be particularly advantageous, since even relatively low concentrations (e.g., 5-40 weight % of the total epoxidation reaction mixture) of methanol markedly improve the rate of reaction and epoxide selectivity.

The reaction temperature is not critical, but should be sufficient to accomplish substantial conversion of the olefin to epoxide within a reasonably short period of time. It is generally advantageous to carry out the reaction to achieve as high a hydrogen peroxid conv rsion as possible, preferably at least 50% and desirably at least 90%, consistent with reasonabl selectivities. The optimum reaction temperature will be influenced by catalyst activity, olefin reactivity, reactant concentrations, and typ of solvent employed, among oth r factors, but typically will be in a range of from about 0°C to 150°C (m re preferably, from about 25°C to 120°C). Reaction

times of from about 10 minutes to 48 hours will typically be appropriate, depending upon the above-identified variables. Although sub-atmosph ric pressures can be employed, the reaction is preferably performed at atmospheric pressure or at elevated pressure (typically, between 1 and 100 atmospheres). Generally, it will be desirable to maintain th reaction components as a liquid phase mixture.

The process of this invention may be carried out in a batch, continuous, or semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a fixed bed, transport bed, stirred slurry, or CSTR reactor. Known methods for conducting metal-catalyzed epoxidations of olefins using hydrogen peroxide will generally also be suitable for use in this process. Thus, the reactants may be combined all at once or sequentially. For example, the hydrogen peroxide may be added incrementally to the reaction zone. Once the epoxidation has been carried out to the desired degree of conversion, the desired epoxide product may be separated and recovered from the reaction mixture using any appropriate technique such as fractional distillation, extractive distillation, liquid-liquid extraction, crystallization, or the like. After separating from the epoxidation reaction mixture by any suitable method such as filtration, the recovered catalyst may be economically re-used in subsequent epoxidations. Similarly, any unreacted olefin or hydrogen peroxide may be separated and recycled. In certain embodiments of the process, the crude epoxidation reaction mixture will also contain an aryl-substituted secondary alcohol or other solvent and possibly a ketone corresponding to the secondary alcohol. After separation of the epoxide from the secondary alcohol and the corresponding ketone, the ketone may be converted back to secondary alcohol by hydrogenation. For example, the ketone may be reacted with hydrogen in the presence of a transition metal hydrogenation catalyst. Hydrogenation reactions of this type are well known to those skilled in the art. The secondary alcohol may also be dehydrated using known methods to yield valuable alkenyl products such as styrene.

From the foregoing description, one skilled in the art can readily ascertain the essential characteristics of this invention, and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages, conditions, and embodiments.

The following examples further illustrate the process of this invention, but are not limitative of the invention in any manner whatsoever.

EXAMPLE 1

This example illustrates the preparation of a titanium-rich silicalite composition suitable for use in the epoxidation process of this invention and having an MFI crystal structure (topology). A "Teflon" beaker was charged with tetraethyl orthosilicate (Aldrich; 122 g; 0.59 mole) and then fitted with an overhead stirrer. An aqueous solution of tetrapropyl ammonium hydroxide (Aldrich; 170 mL; 1.0 M) was added over a 30 min. period and the resulting solution stirred for an additional 30 min. period after addition was completed. A solution of titanium n-butoxide (11.6 g; 0.034 mole) in isopropanol (75 mL) was subsequently added over 45 min. and the mixture stirred for an additional 1.5 hours. Water (150 mL) was thereafter added over a 30 min. period. After transferring to a titanium autoclave, the solution was stirred for 65 hours at 160°C (78 psig; autogenous). The resulting milky product was removed and the fine solids separated by centrifugation. The centrifuged solids were washed three times with water (300 mL portions), with the washed solids being collected by centrifugation, and then dried at 100°C for 2 hours. The dried solids were subsequently calcined at 550°C (the temperature being increased at 10°C/min.) for 5 hours. The calcined titanium-rich silicalite catalyst thus obtained had an x-ray diffraction pattern consistent with the presence of an MFI crystalline phase. Elemental analysis found 44 weight percent Si and 5.1 weight percent Ti (Si:Ti mole:mole=15:1), corresponding to the empirical formula:

$$xTiO_2 \cdot (1 - x)SiO_2$$

wherein x = 0.06.

EXAMPLE 2

This example illustrates a procedure for preparing a titanium-rich silicalite composition useful as an epoxidation catalyst in the process of this invention and having an MEL topology.

The procedure described in Example 1 was repeated, but using tetrabutyl ammonium hydroxide (Aldrich; 170 mL; 1.0 M) in place of the tetrapropyl ammonium hydroxide. The calcined titanium-rich silicalite catalyst obtained had an x-ray diffraction pattern consistent with the presence of an MEL crystalline phase. Elemental analysis found 45 weight p rc nt silicon and 4.9 w ight percent titanium (Si:Ti mole:mol =16:1), corre ponding to th mpirical formula:

$$xTiO_2 \cdot (1 - x)SiO_2$$

wherein x = 0.06.

EXAMPLE 3

A titanium-rich silicalite catalyst containing an MFI crystalline phas and 4.4 weight percent titanium was prepared in accordance with the procedure described in Thangaraj et al., J. Catal., **130**, 1(1991). The catalyst (0.73 g) was then charged to a 300 mL glass-lined autoclave together with methanol (25 mL) and then propylene (16 mL; 0.20 mole). The autoclave was equipped with a "Teflon" stir shaft and blade and a "Teflon" tape-wrapped thermowell. After heating the autoclave to 75°C using an external heating coil, an oxidant mixture containing α-methyl benzyl alcohol, acetophenone, 5.15% hydrogen peroxide, and a minor amount of water (total of 100 mL) which had been prepared by air oxidation of α-methyl benzyl alcohol was then fed into the autoclave over a 15 minute period while constantly stirring the autoclave contents. During the addition, the reaction exothermed to 85°C. The reaction mixture was stirred an additional 30 minutes after addition was completed. After cooling in an ice bath, the contents of the autoclave were analyzed for hydrogen peroxide by iodometric titration and for propylene oxide by gas chromatography. The results obtained were as follows:

Final H_2O_2 concentration = 0.11% (0.0040 mole)
H_2O_2 conversion = 97%
Propylene oxide produced = 0.12 mole
Selectivity to propylene oxide (based on hydrogen peroxide) = 84%

Selectivity to propylene oxide based on propylene was at least 99%, with a total of less than 1% selectivity to propylene glycol and propylene glycol methyl ethers.

EXAMPLE 4

A 300 mL autoclave was charged with the same titanium-rich silicalite catalyst used in Example 3 (varying amounts), methanol, and propylene as described in Example 3. A mixture of α-methylbenzyl alcohol (70 mL), acetophenone (30 mL), and aqueous 50% hydrogen peroxide (10 mL) was stirred with 30 g $MgSO_4$, filtered, and then fed into the autoclave (preheated to 80°C using external heating coils) over 38 seconds using an Isco pump attached to the autoclave. The autoclave was open to a reservoir of liquid propylene to obtain pseudo-first order conditions. The temperature was maintained at 80°C throughout the reaction by internal "Teflon"-lined coils. Samples were removed at 4 minute intervals over 20 minutes and titrated for hydrogen peroxide to obtain the rate data shown below.

Amount of Catalyst (g)	Ti (ppm)	Rate (hr^{-1})
0.73	229	0.58
0.35	109	0.29
0.23	73	0.19

The rate of reaction was found to be extremely fast and proportional to the titanium concentration in the mixture.

EXAMPLE 5

This example demonstrates the use of methanol as a solvent in accordance with the process of the invention. An autoclave equipped as described in Example 3 was charged with methanol (25 mL) and the same titanium-rich silicalite catalyst (0.73 g) employed in Example 3, followed by liquid propylene (16 mL; 0.20 mole). An attached Isco pump was charged with 100 mL of a solution prepared by mixing methanol (90 mL) and 50% aqueous hydrogen peroxide (10 mL; 0.15 mole H_2O_2). The reactor was heated to 63°C using an external heater, at which point the solution in the Isco pump was added over a period of 15 minutes. During the addition, the contents of the reactor reached a temperature of 78°C due to the exothermic reaction. After stirring for 30 minutes at 78°C after addition was completed, the autoclave was cooled with an ice bath and vented. Analysis of the reaction mixture was performed as described in Example 3. The results obtained were as follows:

Final H_2O_2 concentration = 0.25% (0.0092 mole)
H_2O_2 conversion = 94%
Propylen xid produced = 0.12 mol
Selectivity to propylene oxide (based on hydrog n peroxid) = 87%

EXAMPLE 6

This xample illustrates the poxidation of allyl alcohol in accordance with the invention. A flask was charg d with methanol (18 mL), 50% aqueous hydrogen peroxide (2.8 mL; 0.041 mol H_2O_2), allyl alcohol (3.5 mL; 0.051 mole), and the same titanium-rich silicalite catalyst used in Example 3 (0.25 g) and fitted with a reflux condenser. The reaction mixture was heated at 62°C for 4.5 hours and then analyzed by iodometric titration and gas chromatography. The results were as follows:
Final H_2O_2 concentration = 0.42% (0.003 mole)
H_2O_2 conversion = 93%
Glycidol produced = 0.029 mole
Selectivity to glycidol (based on hydrogen peroxide) = 76%

The high selectivity to glycidol was unexpected in view of the teaching of the prior art that the reaction of hydrogen peroxide with allyl alcohol in the presence of a titanium silicalite containing a low level of titanium (U.S. Pat. No. 4,410,501; Example 10) yields glycerin and not glycidol.

EXAMPLE 7

A titanium-rich silicalite catalyst having a Si:Ti molar ratio of 10 is prepared in accordance with the teachings of Thangaraj et al., J. Catal. **130**, 1(1991). The procedure of Example 3 is repeated using this catalyst with the exception that the amount of catalyst is reduced to 0.50 g and the propylene is replaced with allyl chloride (19.3 g; 0.20 moles). Epichlorohydrin is the expected product.

EXAMPLE 8

A titanium-rich silicalite catalyst having a Si:Ti molar ratio of 22 is prepared in accordance with the teachings of Thangaraj et al., J. Catal. **130**, 1(1991). The procedure of Example 3 is repeated using this catalyst with the exception that the amount of catalyst is increased to 1.0 g and the propylene is replaced with styrene (20.8 g; 0.20 moles). Styrene oxide is the expected product.

EXAMPLE 9

A titanium-rich silicalite catalyst having a Si:Ti molar ratio of 17 is prepared in accordance with the teachings of Thangaraj et al., J. Catal. **130**, 1 (1991). The procedure of Example 3 is repeated using this catalyst, with the exception that propylene is replaced with cyclohexene (16.4 g; 0.20 mole) and the reaction temperature is increased to 90°C. The expected product is cyclohexene oxide.

EXAMPLE 10

The procedure of Example 3 is repeated with the exception that the propylene is replaced with ethylene (5.6 g; 0.20 moles) and the α-methyl benzyl alcohol and acetophenone of the oxidant mixture are replaced by an equal volume of isopropanol. Ethylene oxide is the expected product.

EXAMPLE 11

The procedure of Example 3 is repeated with the exception that the propylene is replaced with 2,3-dimethyl-1-butene (16.8 g; 0.20 moles), the methanol, α-methyl benzyl alcohol, and acetophenone are replaced by an equal volume of t-butyl alcohol, and the reaction temperature is reduced to 50°C. The expected product is 2,3-dimethyl-1-butene oxide.

EXAMPLE 12

The procedure of Example 3 is repeated with the exception that the propylene is replaced by allyl phenyl ether (26.8 g; 0.20 mole) the reaction temperature is increased to 100°C, and the mixture is stirred for 60 minutes after addition of the oxidant mixture is completed. The expected product is phenyl glycidyl ether.

EXAMPLES 13-14

Thes xampl s d monstrat that s lectivity to poxid in an olefin poxidation reaction is not adv rsely

affected by the use of a titanium-rich silicalite catalyst, contrary to the expectation of the prior art teachings in this field.

An autoclave equipped as described in Exampl 3 was charged with methanol (25 mL), propylene (16 mL; 0.20 mol), and a titanium-rich silicalite catalyst having an MFI topology and containing 4.4 weight % titanium (0.73 g). The contents of the autoclave were heated to 80°C before adding a mixture (100 mL) of α-methyl benzyl alcohol (70 weight %), acetophenone (25 weight %), and hydrogen peroxide (5 weight %; 0.14 mole) over a 38 sec. period. The autoclave was open to a reservoir of liquid propylene. The reaction mixture was stirred for 45 minutes at 80°C , yielding the results shown in Table I (Example 13).

The procedure described above was repeated, but with the substitution of a conventional titanium silicalite catalyst having an MFI topology and containing only 1.4 weight percent titanium (Comparative Example 14).

TABLE I

Ex. No.	H_2O_2 Conversion, %	Epoxide Selectivity, %
13	97	78
14*	94	80

*Comparative example

Contrary to the expectation of the prior art, which teaches that poorer yields of epoxide products will result if a silicalite containing a relatively high titanium concentration is used, the practice of the process of this invention was found to produce epoxide at a selectivity equivalent to that obtained using a conventional silicalite epoxidation catalyst having a low titanium content.

Claims

1. A process for producing an epoxide by contacting an olefin with a hydrogen peroxide source in the presence of a titanium silicalite zeolite as catalyst characterised in that the zeolite has a Si:Ti molar ratio in the lattice framework thereof of from 8:1 to 23:1.

2. A process as claimed in claim 1 wherein the crystalline titanium silicalite zeolite has an MFI or MEL topology.

3. A process as claimed in claim 1 or claim 2 wherein an organic solvent is additionally present during said contacting.

4. A process as claimed in claim 3 wherein said organic solvent is an alcohol.

5. A process as claimed in claim 4 wherein said organic solvent is selected from methanol, a,methylbenzyl alcohol, isopropyl alcohol, cyclohexanol, and mixtures thereof.

6. A process as claimed in any one of claims 1 to 5 wherein said titanium silicalite zeolite is prepared using a solution of titanium tetrabutoxide dissolved in an anhydrous alcoholic medium.

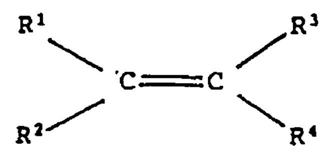
7. A process as claimed in any one of claims 1 to 6 wherein said titanium silicalite zeolite is prepared using a quaternary ammonium salt selected from tetrapropyl ammonium hydroxide, tetrabutyl ammonium hydroxide, methyltributyl ammonium hydroxide, trimethyl ethanol ammonium hydroxide, tetramethyl ammonium hydroxide, and mixtures thereof.

8. A process as claimed in any one of claims 1 to 7 wherein the hydrogen peroxide source is produced by oxidation of an aryl-substituted secondary alcohol with molecular oxygen.

9. A process as claimed in claim 8 wherein said organic solv nt is an aryl-substituted secondary alcohol r a mixture th reof with m thanol.

10. A process as claimed in any one of claims 1 to 9 wherein the process is effected at a temperature of from 0°C to 150°C.

11. A process as claimed in any one of claims 1 to 10 wherein th lefin has the general formula



wherein R^1, R^2, R^3, and R^4 are the same or different and are selected from hydrogen, C_1-C_{20} alkyl, C_7-C_{20} aryl alkyl, C_{54}-C_{12} cycloalkyl, C_6-C_{20} alkyl cycloalkyl, and C_6-C_{20} aryl.

12. A process as claimed in any one of claims 1 to 10 wherein the olefin is selected from ethylene, propylene, 1-butene, 2-butene, 1-pentene, 2-pentene, allyl alcohol, allyl chloride, styrene, cyclohexene, allkyl phenyl ether, norbornene, isoprene, butadiene, isobutylene, 1-octene, vinyl cyclohexane and methallyl alcohol.

13. A process as claimed in any one of claims 1 to 12 wherein the amount of titanium silicalite zeolite is from 0.01 to 10 grams per mole of olefin.

14. A process as claimed in any one of claims 1 to 13 wherein said process is conducted at a pressure of between 1 and 100 atmospheres.

15. A process as claimed in any one of claims 1 to 14 wherein the Si:Ti molar ratio is from 9.5:1 to 18:1.

16. A process as claimed in any one of claims 1 to 15 wherein the molar ratio of olefin:hydrogen peroxide source is from 1:10 to 10:1.

17. A process as claimed in any one of claims 1 to 16 wherein said zeolite has been treated with an acid-neutralizing agent selected from alkaline substances and silylating agents.

18. A process as claimed in claim 1 for producing propylene oxide comprising contacting propylene with hydrogen peroxide at a temperature of from 25°C to 120°C in the presence of an alcohol solvent and a titanium silicalite zeolite having a Si:Ti molar ratio in the lattice framework of said zeolite of from 9.5:1 to 18:1 and an MEL or MFI topology, the amount of titanium silicalite zeolite being from 0.01 to 10 grams per mole of olefin and the molar ratio of olefin:hydrogen peroxide being from 1.05:1 to 1.75:1.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 568 336 A3

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number: 93303310.2

(51) Int. Cl.[5]: C07D 301/12

(22) Date of filing: 28.04.93

(30) Priority: 30.04.92 US 876772

(43) Date of publication of application: 03.11.93 Bulletin 93/44

(84) Designated Contracting States: AT BE DE ES FR GB IT NL

(88) Date of deferred publication of search report: 16.03.94 Bulletin 94/11

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(54) **Epoxidation process using titanium-rich silicalite catalysts.**

(57) Olefins are epoxidized by hydrogen peroxide in the presence of a crystalline titanium silicalite zeolite catalyst having a Si:Ti molar ratio in the lattice framework of from 8:1 to 23:1. High yields of epoxides with minimal non-selective loss of either hydrogen peroxide or olefin are realized.

EP 0 568 336 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 3310 2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
Y	LA CHIMICA & L'INDUSTRIA vol. 72, no. 7 , 1990 , MILAN (IT) pages 610 - 616 U. ROMANO ET AL. 'Selective oxidation with Ti-silicalite' * the whole document *	1-18	C07D301/12
D,Y	JOURNAL OF CATALYSIS vol. 130 , 1991 , NEW-YORK (USA) pages 1 - 8 A. THANGARAJ ET AL. 'Catalytic Properties of Crystalline Titanium Silicalites. I. Synthesis and Characterization of Titanium-Rich Zeolites with MFI Structure' * the whole document, particularly paragraph bridging pages 6 and 7*	1-18	
Y	JOURNAL OF CATALYSIS vol. 131 , 1991 , NEW-YORK (USA) pages 294 - 297 A. THANGARAJ ET AL. 'Catalytic Properties of Crystalline Titanium Silicalites. II. Hydroxylation of Phenol with Hydrogen Peroxide over TS-1 Zeolites' * the whole document, particularly page 294, paragraph bridging left- and right-hand columns	1-18	TECHNICAL FIELDS SEARCHED (Int.Cl.5) C07D B01J
Y	JOURNAL OF CATALYSIS vol. 131 , 1991 , NEW-YORK (USA) pages 394 - 400 A. THANGARAJ ET AL. 'Catalytic Properties of Crystalline Titanium Silicalites. III. Ammoximation of Cyclohexanone' * the whole document, particularly paragrap bridging pages 395 and 396	1-18	

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 January 1994	Allard, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 30 3310

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
E	EP-A-0 568 337 (ARCO CHEMICAL TECHNOLOGY) 3 November 1993 * the whole document, particularly page 6, lines 29-35 -----	1-18	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)

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EPO FORM 1503 03.82 (P04C01)

(19) Europäisches Patentamt
European Patent Offic
Office européen des brevets

(11) Publication number: 0 230 949
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 87100625.0

(22) Date of filing: 19.01.87

(51) Int. Cl.[4]: C 07 D 301/12
B 01 J 29/04
//C07D303/04, C07D303/08

(30) Priority: 28.01.86 IT 1920786
28.01.86 IT 1920986

(43) Date of publication of application:
05.08.87 Bulletin 87/32

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

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(54) A process for the epoxydation of olefinic compounds.

(57) A process for the epoxidation of olefinic compounds comprising reacting said compounds with hydrogen peroxide introduced as such or produced by substances under the reaction conditions, in the presence of synthetic zeolites containing titanium atoms corresponding to the general formula:

$$x\, TiO_2 \,.\, (1-x)\, SiO_2$$

wherein x is in the range of from about 0.0001 to about 0.04, and optionally, in presence of one or more solvents, at a temperature in the range of from about 0 to about 150°C. and at a pressure of from about 1 to about 100 atm. The synthetic zeolites are treated with alkaline substances before and/or during their use in the reaction, or alternatively the synthetic zeolites are acid neutralized with a compound such as $X-Si-(R)_3$ where X is selected from Cl, Br, I, $CH_3CON-Si-(CH_3)_3$, $CF_3COON-Si-(CH_3)_3$, $(R)_3-Si-NH$, and an imidazolyl group wherein R is selected from an alkyl, aryl or alkylaryl group.

EP 0 230 949 A2

Croydon Printing Company Ltd.

FIELD OF THE INVENTION

The present invention is directed to a process for the epoxidation of olefinic compounds with hydrogen peroxide introduced as such or produced by substances under the reaction conditions, in presence of synthetic zeolites containing titanium atoms, wherein the synthetic zeolites are [acid] neutralized < as to their acidity>.

BACKGROUND OF THE INVENTION

European Patent Application No. 100119 discloses a process for the epoxidation of olefinic compounds, starting from olefins and hydrogen peroxide or substances which can produce hydrogen peroxide under the reaction conditions, wherein the catalyst is a synthetic zeolite containing titanium atoms (titanium-silicalite) corresponding to the general formula:

$$x\ TiO_2.(1-x)SiO_2$$

wherein x is in the range of from 0.0001 to 0.04. The catalyst is chosen from among catalyst compositions having the following molar ratios of reactants:

Molar Ratios of Reactants		Preferred Molar Ratios
SiO_2/TiO_2	5-200	35-65
OH^-/SiO_2	0.1-1.0	0.3-0.6
H_2O/SiO_2	20-200	60-100
Me/SiO_2	0.0-0.5	0
RN^+/SiO_2	0.1-2.0	0.4-1.0

wherein RN^+ represents an organic nitrogen cation derived from the organic base utilized for the preparation of titanium-silicalite (TS-1). Me is an alkaline ion, preferably chosen from among Na or K.

The final TS-1 product is a composition having the formula $x\ TiO_2.(1-x)SiO_2$ wherein x is in the range of from 0.0001 to 0.04, preferably from 0.01 to 0.025.

TS-1 is silicalite type product wherein titanium atoms vicariate the silicon atoms. A further and more precise identification of the titanium-silicalite which is used as a catalyst is set forth in said European patent application and in Belgian Patent No. 886812.

The titanium-silicalite catalyst may be utilized in the expoxidation reaction as a dust or preferably in the form of granules having a particle size of from 5 to 1000 µm wherein the granules are made of zeolitic crystals bound by a suitable inorganic binder, preferably oligomeric silica.

It has been observed that in the synthesis of epoxified compounds derived from olefins and hydrogen peroxide with said catalysts in a protic medium (such as water, alcohol and mixtures thereof), selectivity of the desired epoxide is generally very high. Yet some amount of by-products from solvolysis is always present, especially when working at high temperatures. This results in increased costs because of the lower yield of the epoxide and because of the need to separate the by-products from the reaction.

It has surprisingly been found that it is possible to significantly reduce the amount of the aforesaid undesirable by-products by treating the catalyst prior to the reaction or during the reaction with suitable acid neutralizing agents to neutralize acid groups which are on the catalyst surface.
The catalyst can also be treated with a substance which can neutralize catalyst acidity using an inert group bound to a polar group which is easily displaced by reaction with SiOH.

The acidity of non-treated titanium-silicalite is already very low which is due to the presence of some SiOH groups, especially on the outer surface of the crystals or in the lattice defects. However, the presence of even a small number of acid groups results in the production of unacceptable amounts of by-products due to the solvolysis reaction described above.

SUMMARY OF THE INVENTION

The process of the epoxidation of olefinic compounds in accordance with the present invention comprises reacting in a reaction zone one or more olefinic compounds with hydrogen peroxide or substances which produce hydrogen peroxide under the reaction conditions, in presence of a catalyst comprised of a synthetic zeolite (titanium-silicalite), wherein the catalyst is, prior to the epoxidation reaction, neutralized as to its acidity by a compound of the formula $X-Si-(R)_3$ wherein X is selected from Cl, Br, I, $CH_3CON-Si-(CH_3)_3$, $CF_3COON-Si-(CH_3)_3$, $(R)_3-Si-NH$, and an imidazolyl group, wherein R is an alkyl, aryl or alklaryl group wherein the alkyl group has from 1 to 4 carbon atoms.

Catalyst neturalization may also be accomplished before and/or during the reaction, with basic substances which are water soluble. Such basic substances may be chosen from among strong bases, such as NaOH, KOH, and weak bases such as NH_4OH, Na_2CO_3, $NaHCO_3$, Na_2HPO_4 and analogous potassium and lithium salts including K_2CO_3, Li_2CO_3, $KHCO_3$, $LiHCO_3$ and K_2HPO_4, alkaline and/or alkaline-earth salts of carboxylic acids having from 1 to 10 carbon atoms and alkaline and/or alkaline earth alcoholates, having from 1 to 10 carbon atoms.

In a batchwise epoxidation reaction,

neutralization of the catalyst with basic substances, which are water soluble, is carried out by forming a slurry of the catalyst in a diluted solution of the neutralizing agent chosen among those mentioned above and stirring the slurry at a temperature of from about room temperature to about 100°C. for a few minutes. The catalyst is then removed and thoroughly washed to completely remove excess base. After drying, the catalyst is utilized for the epoxidation of the olefin, with surprisingly high selectivity to epoxide. In the event the epoxidation reaction is performed in a continuous flow (fixed bed reactor, CSTR reactor, i.e., continuous flow stirred tank reactor), it is sufficient to add to the hydrogen peroxide feed from about 0.0001 to about 0.1% by weight of a neutralizing agent which is soluble in the medium and weakly basic, (e.g., CH_3COONa, Na_2HPO_4, Na_2CO_3 and the like) in order to prevent deterioration of the catalyst over time. In this way, it is possible to prevent indefinitely the catalyst from initiating the undesireable solvolysis by product formation reaction. The amount of the neutralizing agent which is employed depends on the nature of the reaction medium, the space velocity, and the temperature.

Alternatively, neutralization of the catalyst is conducted by reacting the compounds of the general formula ($X-Si-(R)_3$) with the titanium-silicalite.

The reaction may be carried out in an inert solvent such as acetonitrile, chloroform, pyridine and dioxane and the like with or without an organic base such as pyridine or at least one tertiary amine. In accordance with this procedure, it is possible to transform all of the SiOH groups present on the surface of the titanium-silicalite, to $SI-O-Si-(R)_3$ groups which

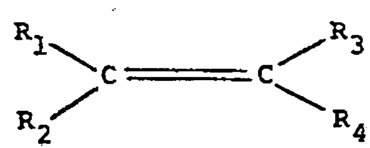
are chemically inert to solvolysis of the epoxy ring.

The epoxidation reaction between the olefin and hydrogen peroxide is performed at a temperature of from about 0 to about 150°C. and at a pressure of from about 1 to about 100 atm with or without the presence of one or more solvents.

The epoxidation reaction may be performed in batch or in a continous flow on a fixed bed, or in a CSTR reactor in a monophase or biphase system.

The catalyst is stable under the reaction conditions and may be completely recovered and reused. Examples of the solvents which can be used include polar compounds such as alcohols, ketones, esters, ethers, glycols, with the number of carbon atoms not too high, preferably less than or equal to 6 carbon atoms. Preferred examples of the alcohols are methanol and terbutanol. A preferred example of a ketone is acetone.

The olefinic compounds that may be epoxidized according to the present invention include compounds having the general formula:



wherein R_1, R_2, R_3, and R_4 may be the same or different and are selected from H and an alkyl, alkylaryl, cycloalkyl and alkylcycloalkyl group, wherein the alkyl group has from 1 to 20 carbon atoms, the alkylaryl group has from 7 to 20 carbon atoms, the cycloalkyl group has from 6 to 10 carbon atoms and the alkylcycloalkyl group

has from 7 to 20 carbon atoms. The R_1, R_2, R_3 and R_4 groups may be coupled together to form saturated or unsaturated rings (e.g., R_1, R_2 may be coupled together and/or R_3 and R_4 may be coupled together).

The R_1, R_2, R_3, and R_4 groups described above may be substituted with at least one substituent selected from halogen (preferably Cl, Br and I), nitro, sulfonic, carbonilic, oxydrilic, carboxylic and ether groups. By way of example, the olefins that may be epoxidized in accordance with the present invention are, e.g., ethylene, propylene, allyl chloride, butene-2, butene-1, octene-1, 1-tridecene, mesityl oxide, isoprene, cyclooctene and cyclohexene and the like.

It is desirable to conduct the epoxidation reaction at a pressure higher than atmospheric pressure if gaseous olefins are used, in order to make them soluble or liquid under the reaction conditions. Operating at temperatures higher than 0°C. influences the kinetics of the reaction although the reaction proceeds rapidly even at temperatures near 0°C.

The following examples are directed to particular embodiments of the present invention . It should be noted, however, that the examples are merely illustrative and are not meant to limit the invention as set forth in the claims forming part of the application.

EXAMPLE 1

1154 g of tetraethylorthosilicate were added under strong stirring to 1232 g of a 12% by weight tetrapropylammonium hydroxide solution and heated for one hour at 60°C. 5049 g of demineralized water were added to the heated solution and stirring was continued

for another hour until a clear solution was obtained. 3000 g of titanium-silicalite was carefully slurried into the clear solution. The titanium-silicalite is prepared according to the method disclosed in European patent application 100119 incorporated herein by reference.

The resulting milky slurry was fed to a spray-dryer (Niro-Atomizer, disk-atomizer, inlet air temperature 300°C., outlet air temperature 120°C., chamber diameter 1.5m) obtaining dense microspheres having a mean diameter of about 20 μm.

The atomized catalyst was put in a muffle and calcined for four hours at 550°C. 200 g of atomized titanium-silicalite thus prepared were slurried in 1 liter of distilled water containing 10 g of sodium acetate. The slurry was heated at reflux temperature for 10 minutes and then filtered. The aforementioned treatment was repeated a second time in the same way with the same reactants. The resulting product was filtered again and then washed many times with hot distilled water. Then the washed catalyst was dried in a stove and then in a muffle at 550°C.

EXAMPLE 2

150 g of titanium-silicate prepared in the same manner as in Example 1, were slurried in 500 ml of water containing 5 g of Na_2HPO_4. The slurry was heated at reflux temperature for 15 minutes. The heated slurry was filtered and the treatment was repeated a second time. Thereafter the resulting product was washed repeatedly as described in Example 1.

Similar dilute solutions using other bases may be employed in the same manner to prepare highly

active and selective epoxidation catalysts.

EXAMPLE 3

195 g of distilled water, 280 g of methanol and 4.5 g of catalyst prepared as described in Example 1, were loaded into a one liter steel autoclave provided with a mechanical stirrer, a thermostatic system and means for maintaining constant pressure. 56 g of a 32% by weight hydrogen peroxide solution were loaded in a tank connected to the autoclave. After thermostating at 40°C. and pressurizing with propylene under stirring at 6 atm (constant during the entire reaction), hydrogen peroxide was added in a single step to the slurry in the autoclave. Samples were taken at set time intervals and anyalyzed.

Hydrogen peroxide was titrated by iodometry and the reaction products were analyzed by gas chromatography, utilizing a column filled with Poropak PS, 1.8m long. The results are shown in Table 1.

EXAMPLE 4

The procedure of Example 3 was followed using the same quantities of reactants, except that 4.5 g of the titanium-silicalite atomized as such without treatment with a base was used to carry out epoxidation of propylene. The results are shown in Table 1. As shown in Table 1, the results obtained using titanium-silicalite, without treatment with a base were not as good as those obtained with the base treated catalyst.

TABLE 1

	Example 3			Example 4		
t(min)	H_2O_2 (M/Kg)	PO (M/Kg)*	Others (M/Kg)**	H_2O_2 (M/Kg)	PO (M/Kg)*	Others (M/Kg) *
4'	0.744	0.245	0.001	0.661	0.320	0.007
12'	0.421	0.562	0.004	0.371	0.590	0.020
24'	0.225	0.757	0.008	0.185	0.753	0.052
40'	0.051	0.917	0.021	0.058	0.865	0.067

*PO = Propylene oxide.

**Propylene glycol, 1-methoxy-2-hydroxypropane, 2 methoxy-1-hydroxypropane.

EXAMPLE 5

450 g of methanol, 100 g of octene-1, 5 g of catalyst prepared as in Example 2 were loaded in a 1 liter autoclave, provided with a mechanical stirrer, thermostatic system and constant pressure control. 50 g of a 34% by weight solution of H_2O_2 were loaded in the tank connected to the autoclave. After thermostating at 45°C., under strong stirring, hdyrogen peroxide was added to the mixture of the other reactants. Samples were drawn at regular time intervals and analyzed.

Hydrogen peroxide was determined through iodometry and the reaction products determined by gas liquid chromatography, after 1 hour of reaction time:

H_2O_2 Conversion	88%
Octene Conversion	49.2%
Selectivity to 1,2-epoxyoctane	98%

EXAMPLE 6

400 g of methanol, 100 g of allyl chloride, 10 g of catalyst prepared as in Example 1, were put in an autoclave as in Example 5. 70 g of a 34% by weight solution of H_2O_2 were loaded into the tank. The reaction was carried out at 60°C. for 30 minutes. Hydrogen peroxide and allyl chloride conversion and selectivity to epichlorohydrin was measured in the same general manner described in Example 5.

H_2O_2 Conversion	93%
Allyl Chloride Conversion	49.7%
Selectivity to Epichlorohydrin	97.5%

EXAMPLE 7

21 g of titanium-silicalite prepared in the same manner as in Example 1, calcined at 550°C. and cooled in a dry atmosphere, were slurried in a mixture of 20 cc of

anhydr us pyridine, 9 cc of trimethylchlorosilane and 3 cc of hexamethyldisilazane. The slurry was kept under stirring at 50°C. for 2 hours. The solid was then filtered, washed twice with 10 cc of anhydrous pyridine, twice with 10 cc of acetonitrile, three times with 10 cc of water and then thoroughly dried in vacuo.

EXAMPLE 8

1154 g of tetraethylorthosilicate were added under strong stirring to 1232 g of a 12% by weight solution of tetrapropylammonium hydroxide and heated for 1 hour at 60°C. 5049 g of demineralized water were then added to the heated mixture and stirring was maintained for another hour to thereby obtain a clear solution. 3000 g of titanium-silicate, prepared according to Example 1 were carefully slurried into the clear solution.

The resulting milky slurry was fed to a spray-dryer (Niro Atomizer, disk atomizer; inlet air temperature 300°C.; outlet air temperature 120°C.; chamber diameter 1.5 m) obtaining dense microspheres having a mean diameter of about 20 µm.

The atomized catalyst was put in a muffle and calcined for four hours at 550°C. 12g of the resulting titanium-silicate thus prepared were treated at 80°C. with 6 cc of bis(trimethylsilyl)acetamide in 10 cc of anhydrous acetonitrile for 2 hours.

The thus obtained solid product was filtered, washed many times with hot acetonitrile, and then methanol. The washed product was dryed in a stove at 100°C.

EXAMPLE 9

In a similar manner as described in Example 8,

10 g of titanium-silicate was treated with 3 cc of hexamethyldisilazane in 10 cc of acetonitrile. After refluxing for 2 hours, the resulting product was filtered, washed many times with acetonitrile and finally washed three times with water. The washed product was then dryed in vacuo.

EXAMPLE 10

190 g of distilled water, 280 g of methanol and 4.5 g of titanium-silicalite were loaded into a 1 liter steel autoclave, provided with a mechanical stirrer, thermostatic system and constant pressure control. 52 g of a 34% by weight solution of hydrogen peroxide were loaded in a tank connected to the autoclave.

After thermostating at 40°C. and pressuring with propylene, under stirring, at a constant pressure of 6 atm, the entire amount of hydrogen peroxide was added in a single step to the contents of the autoclave. Samples were drawn at regular intervals and analyzed. Hydrogen peroxide was titrated by iodometry and the reaction products were analyzed by gas-liquid chromatography on a column filled with Poropak PS, 1.8 m long. The results are shown in Table 2.

EXAMPLE 11

A test was carried out in the same way and with the same reactants as those in Example 10, except that 4.5 g of titanium-silicalite treated in the same manner as Example 7 were loaded into the autoclave. The results are shown in Table 2. As shown in Table 2, the selectivity to the desired epoxide was significantly greater than the selectivity using the untreated catalyst described in Example 10.

	Example 10			Example 11		
t(min)	H_2O_2 (M/Kg)	PO (M/Kg)*	Others (M/Kg)**	H_2O_2 (M/Kg)	PO (M/Kg)*	Others (M/Kg)
4'	0.660	0.320	0.006	0.783	0.208	0.002
12'	0.371	0.590	0.020	0.481	0.503	0.008
24'	0.186	0.753	0.054	0.235	0.747	0.009
40'	0.058	0.865	0.067	0.089	0.881	0.020

*PO = Propylene oxide.

**Propylene glycol, 1-methoxy-2-hydroxypropane, 2 methoxy-1-hydroxypropane.

EXAMPLE 12

450 g of methanol, 100 g of octene-1, and 5 g of catalyst prepared as in Example 8, were loaded into a one liter autoclave, provided with a mechanical stirrer and a thermostatic system and a constant pressure control. 50 g of a 34% by weight solution of H_2O_2 were loaded in a tank connected to the autoclave. After thermostating at 45°C. under strong stirring, hydrogen peroxide was added to the mixture of the other reactants. Samples were drawn at regular intervals and analyzed.

Hydrogen peroxide was titrated by iodometry and the reaction products analyzed by gas-liquid chromatography after one hour.

H_2O_2 Conversion	85%
Octene Conversion	47.5%
Selectivity to 1,2 epoxyoctane	97.5%

EXAMPLE 13

The reaction was carried out in the same manner and with the same equipment as described in Example 12. 400 g of methanol, 100 g of allyl chloride, and 10 g of the catalyst prepared as in Example 9 were added to the autoclave. 70 g of a 34% by weight solution of H_2O_2 were loaded in the tank. The reaction was carried out at 60°C. for 30 minutes.

H_2O_2 Conversion	94%
Allylchloride Conversion	50.1%
Selectivity to Epichlorohydrin	98%

CLAIMS

1) A process for the epoxydation of olefinic compounds comprising reacting in a reaction zone one or more olefinic compounds with hydrogen peroxide introduced as such or produced by substances which can produce it at the reaction conditions, in presence of a synthetic zeolite as catalyst, containing titanium atoms corresponding to the general formula $x\ TiO_2 \cdot (1-x)\ SiO_2$ wherein x is in the range of from 0.0001 to 0.04 and titanium vicariates silicon, characterized in that the catalyst is neutralized, as to its acidity, with neutralizing agents.

2) A process according to claim 1 characterized in that neutralization may occur before and/or during the reaction.

3) A process according to claim 2 characterized in that when neutralization occurs before and/or during the reaction, the neutralizing agents are basic substances which are, at least, hydrosoluble.

4) A process according to claim 3 characterized in that the basic substances are strong bases.

5) A process according to claim 4 characterized in that the strong bases are NaOH or KOH.

6) A process according to claim 3 characterized in that the basic substances are weak bases.

7) A process according to claim 6 characterized in that the weak bases are chosen among NH_4OH, Na_2CO_3, $NaHCO_3$, Na_2HPO_4, K_2CO_3, Li_2CO_3, $KHCO_3$, $LiHCO_3$, K_2HPO_4, alkaline and/or alkaline earth salts of carboxylic acids with a number of carbon atoms from 1 to 10 and alkaline and/or alkaline-earth alcoholates with a number of carbon atoms from 1 to 10.

8) A process according to Claim 2 characterized in that when neutralization occurs before the reaction, the neutralizing agents are compounds of the type $X\text{-}Si\text{-}(R)_3$ where X is Cl, Br, I, $CH_3CON\text{-}Si\text{-}(CH_3)_3$, $CF_3COON\text{-}Si\text{-}(CH_3)_3$, R_3SiNH, imidazolyl, and R is an alkyl, aryl, alkylaryl group wherein the alkyl has a number of carbon atoms from 1 to 4.

9) A process according to claim 8 characterized in that neutralization occurs by reacting the compounds of said general formula with

the catalyst in an inert solvent.

10) A process according to claim 9 characterized in that the inert solvent is chosen among acetonitrile, chloroform, pyridine, dioxane, eventually in presence of an organic base.

11) A process according to claim 10 characterized in that the organic base is chosen among pyridine and tertiary amines.

12) A catalyst, for the epoxydation of olefines, which is constituted by a synthetic zeolite containing titanium atoms corresponding to the general formula $xTiO_2 \cdot (1-x) SiO_2$ wherein x is in the range of from 0.0001 to 0.04 and titanium vicariates silicon, characterized in that the surface of the catalyst has Si-O-Si (R_3) groups, R is selected from alkyl, aryl, and alkylaryl wherein the alkyl group has from 1 to 4 carbon atoms, and said surface has substantially no SiOH groups.